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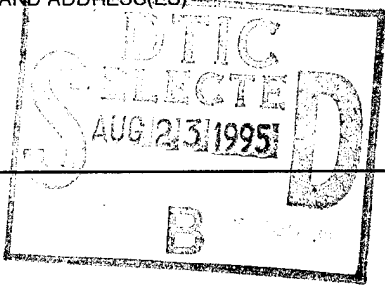
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1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE 15 August 1995	3. REPORT TYPE AND DATES COVERED 6/94 – 5/95

4. TITLE AND SUBTITLE

Evidence for Specific and Non-Specific Adsorption of ClO_4 on Ag(110)

6. AUTHOR(S)

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5. FUNDING NUMBERS

N00014-91-J-1909

R&T Code 4133035

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8. PERFORMING ORGANIZATION REPORT NUMBER

Technical Report No. 4

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

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14. SUBJECT TERMS

Double Layer Modeling, Nonspecific Adsorption, Perchlorate Ion, Silver(110), Metal/Electrolyte Interface

15. NUMBER OF PAGES

19

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	

OFFICE OF NAVAL RESEARCH

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by

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Prepared for Publication

in

University of Washington
Department of Chemical Engineering
Box 351750
Seattle, WA 98195-1750

August, 1995

19950822 028

EVIDENCE OF SPECIFIC AND NON-SPECIFIC ADSORPTION OF PERCHLORATE (ClO$_4$) ON SILVER(110)

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Abstract

The coadsorption of ClO$_4$ with H$_2$O on Ag(110) was studied as a model of anion adsorption at the solid-liquid interface. Thermal desorption spectroscopy, low energy electron diffraction, and high resolution electron energy loss spectroscopy were used to investigate the interactions between perchlorate, water and the metal surface. The vibrational spectrum of adsorbed ClO$_4$ is an indicator of its adsorption geometry. For ClO$_4$ adsorbed on the clean surface, losses at 640, 915, 1020 and 1220 cm^{-1} indicate that adsorption occurs through three oxygen atoms (tridentate) with a symmetry of C$_{3v}$ or lower. When coadsorbed with H$_2$O, the vibrational spectrum resembles that of fully solvated, tetrahedral ClO$_4^-$ (T$_d$ symmetry) with bands at 610, 880 and 1090 cm^{-1}. The increase in symmetry indicates that direct interaction with the metal is lost and is considered evidence for non-specifically adsorbed ClO$_4$ in UHV. The thermodynamic feasibility of this process is also discussed.

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I. INTRODUCTION

Models of the electrochemical interface have been investigated in UHV by various surface-sensitive techniques in order to probe the molecular level interactions between the metal and the electrolyte.[1-8] They often involve anions directly adsorbed to the metal (so-called specific adsorption) prior to the addition of solvent. To model non-specific adsorption requires the formation of a stable ion in the adsorbed layer that is not in contact with the surface. The only known example of a non-specifically adsorbed species in UHV is the formation of hydronium from coadsorbed H and H_2O on the (111) and (100) surfaces of platinum.[7,8] The perchlorate ion is one of the most likely candidates to model the anionic counterpart of this behavior by virtue of its tendency for non-specific adsorption electrochemically and because it can be generated in UHV. Coadsorption of water and perchlorate thus offers the opportunity for direct evidence of non-specific adsorption of an anion in UHV.

Because perchlorate is polyatomic, changes in its internal vibrational modes will reflect changes in its adsorption environment. In potential-dependent infra-red (IR) studies of Pt(111) in perchloric acid solution, a band at 1200-1234 cm^{-1} appears between 575 and 1100 mV NHE (normal hydrogen electrode) in addition to that of the ion in solution at 1100-1119 cm^{-1}.[9] The change from low to high vibrational frequency band represents the change from hydrated, solution phase ClO_4^- to specifically adsorbed ClO_4.

With the bonding of ClO_4 to the metal, the tetrahedral symmetry of the perchlorate ion is lowered to an extent that depends on the number of bonds formed with the metal, which varies from one (monodentate) to two (bidentate) to three (tridentate). For monodentate or tridentate coordination, the T_d symmetry of ClO_4^- would be lowered to C_{3v} if the symmetry of the substrate is ignored, while for bidentate coordination, the symmetry would be lowered further to C_{2v}. Although coordination of a perchlorate

molecule to a metal surface is expected to differ from coordination to a single metal atom, spectra of perchlorate salts of the latter can serve as standards for the vibrations of ClO_4 as a function of symmetry and coordination. The modes observed by IR spectroscopy for $Cu(ClO_4)_2$ and $Cu(ClO_4)_2 \cdot 2H_2O$[10] and by Raman and IR spectroscopy of rare-earth metal perchlorates[11] are shown in Table I, along with those observed for the perchlorate ion in solution.[12] As the symmetry is lowered, the degeneracy of the asymmetric Cl-O stretch is removed and additional vibrational modes appear in the spectrum. The number of observed vibrational modes can then be used to evaluate the symmetry of adsorbed perchlorate and how it is affected by coadsorbed water.

II. EXPERIMENTAL PROCEDURE

The experiments were conducted in stainless steel UHV chamber that has been described previously.[4,6,8] The typical resolution (full width at half-maximum, FWHM) of the high resolution electron energy loss spectrometer (HREELS) was 100 cm⁻¹, and all energy losses are rounded to the nearest 5 cm⁻¹. EELS spectra were collected at a sample temperature of 110 K following adsorption or annealing.

Adsorbed perchlorate was produced by heating perchloric acid, adsorbed at 110 K, to 300 K to remove hydrogen, excess perchloric acid and any coadsorbed water from the surface, as shown in eqn. (1). Estimates of coverage are based on the observed LEED patterns and comparison to previous results.[13]

$$HClO_4 \longrightarrow ClO_{4,a} + 1/2\, H_{2,g} \qquad 300\,K \qquad (1)$$
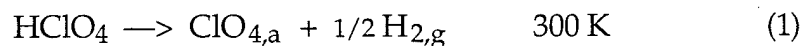
Water and $HClO_4$ vapor were introduced sequentially through a common glass capillary array doser.[14] Dosing was conducted with the array positioned within 2 mm of the sample. H_2O coverages were calculated from integration of the mass spectrometer signal during thermal desorption and calibration using known

standards.[4,15] They are reported in terms of monolayers (ML) of the topmost Ag atoms of the perfect (110) surface: 8.45×10^{14} cm^{-2}.

An approximate measure of work function change was taken from the change in sample bias potential in HREELS required to maximize the intensity of the elastic peak. This method works so long as the region in the vicinity of the sample is free of electric fields. This condition was satisfied by tuning the spectrometer such that a spectrum of the clean surface was obtained without an applied radial deflection of the electron beam as it exited the monochromator or entered the analyzer. Radial deflection of the electron beam changes the direction of the electron beam along a direction normal to the surface. Shifts in work function due to adsorption introduce electric fields around the sample, which deflect the electron beam and degrade the measured spectrum, unless the change in work function is compensated, and a field-free region restored, by changing the sample bias. The reference bias for the clean Ag(110) surface was 0.0 V with respect to ground. A positive sample bias therefore represents an increase in work function and a negative sample bias a decrease in work function with respect to the clean surface.

III. RESULTS

A. Adsorbed ClO$_4$

Fig. 1 shows EEL spectra for adsorbed perchlorate at 110 K. The observed LEED patterns associated with the surface examined in spectra (a) and (c) were (1x1) and c(2x2), respectively. This corresponds to coverages of < 0.2 ML and 0.5 ML, according to previous data.[13] Peaks below 1600 cm^{-1} are due to fundamental modes of perchlorate. Strong peaks are observed at 640, 915 and 1220 cm^{-1} and a weak band is observed at 1020 cm^{-1}. The bias potential was increased from 0.0 V (clean surface) to 1.9 V in spectrum (a), indicating an increase in work function due to adsorbed perchlorate. In spectrum (c), the radial deflection of the beam entering the analyzer was nonzero, so

the change in sample bias could not be used to measure work function.

Above 1600 cm^{-1}, the peaks at 2990 and 3555 cm^{-1} are assigned to O-H stretches of water interacting with perchlorate. The adsorbed water came from the background gas in the UHV chamber and amounted to just 0.04 ML as judged from the thermal desorption peak at 200 K in fig. 2(a). When the ClO_4 coverage was increased to 0.5 ML, desorption of 0.06 ML H_2O, again adsorbed from residual H_2O, occurred at a higher temperature of 220 K, as shown in fig. 2(c). The peak at 2350 cm^{-1} in fig. 1(a) is most likely an overtone of the peak at 1220 cm^{-1}, as it exhibits the same width as the other perchlorate peaks, while the O-H stretching peaks are slightly broader.

B. Coadsorption of ClO_4 and H_2O

Following the thermal desorption curve of fig. 2(a), water was adsorbed at 100 K and the sample heated to 170 K to ensure desorption of any multilayers. For the EELS measurement the sample bias was reduced to 0.1 V, indicating that the work function was close to that of the clean surface. The resulting spectrum, shown in fig. 1(b), is markedly different from that for adsorbed ClO_4 alone. The peak at 200 cm^{-1} is assigned to frustrated translation of H_2O. The 725 cm^{-1} peak is assigned to H_2O libration, but shoulders of this peak at 610 and 880 cm^{-1} are due to contributions from ClO_4 or a combination mode of the frustrated translation and libration. The sharp peaks at 915 and 1220 cm^{-1} seen in (a) have been replaced by a broader feature at 1090 cm^{-1}. A distinct H_2O scissoring mode appears at 1635 cm^{-1}. A broad band at 3545 cm^{-1} dominates the O-H stretching region with a smaller peak at 3000 cm^{-1}. The H_2O thermal desorption in fig. 2(b), measured after the EELS spectrum, shows a single peak at 190 K and an area corresponding to a coverage of 0.62 ML. This places the ratio of H_2O to ClO_4 at greater than three, given the initial perchlorate coverage of less than 0.2 ML mentioned above, and is consistent with previously measured H_2O/ClO_4 ratios.[13]

For 0.5 ML of perchlorate, H_2O was again adsorbed to 0.33 ML at 100 K and the EEL spectrum measured as shown in fig 1(d). In contrast to the results for the lower perchlorate coverage (b), the peaks due to adsorbed ClO_4 at 640, 915 and 1240 cm^{-1} observed for the nominally water-free surface (c) are not removed by coadsorption of H_2O, but the intensities of these three peaks have decreased. Although a librational peak near 725 cm^{-1} is absent in (d) evidence of adsorbed water is seen in the development of the internal H_2O bending and stretching modes, respectively, at approximately 1630 cm^{-1} and in a region extending from 2700 to 3700 cm^{-1} with a peak at 3540 cm^{-1}. Subsequent thermal desorption in fig. 2(d) shows a smaller H_2O desorption peak at 190 K, in comparison to fig. 2(b), and the appearance of a shoulder at 210 K.

IV. DISCUSSION

A. Bonding of ClO_4 to Ag(110)

The electron energy losses of fig. 1 are compared to those of metal perchlorate complexes and ionic perchlorate in Table I. In terms of the number of identifiable bands, the spectrum for the adsorbed perchlorate (without water) compares favorably with those of $Cu(ClO_4)_2 \cdot 2H_2O$ and $M(ClO_4)_3$ where M is a rare-earth metal, indicating C_{3v} symmetry. Good agreement is found between the peak at 1220 cm^{-1} observed for $ClO_4/Ag(110)$ and the Cl-O stretch in the tridentate $M(ClO_4)_3$. Conversely, the 915 cm^{-1} peak agrees better with the Cl-O stretch of the monodentate species. This disagreement suggests that a definitive assignment of the adsorption of perchlorate cannot be made based on the vibrational spectrum alone. For this, additional structural information, such as that provided by LEED and electron stimulated desorption ion angular distribution (ESDIAD), is required.

For 0.1 ML ClO_4, the appearance of two O^+ ESDIAD lobes along the [001] direction were assigned to a bidentate perchlorate adsorbed atop a single Ag atom in the

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trough.[13] At 0.5 ML ClO$_4$, the O$^+$ emission changes to two lobes along the [1$\bar{1}$0] direction, and a bidentate structure rotated 90° from the first was proposed. However, these models are contradicted by the energy loss data which favor either the monodentate or tridentate forms. Fig. 3(a) shows a model that rectifies the differing interpretations of the ESDIAD and HREELS data. For 0.1 ML ClO$_4$ one oxygen atom resides in a (111) site of the trough while the other two reside on ridge atoms. The terminal Cl-O bond is tilted away from the surface normal and toward the [001] direction to give agreement with the ESDIAD data. Fig. 3(b) shows the change in perchlorate adsorption when the ClO$_4$ coverage is increased to 0.5 ML. The perchlorate molecules are adsorbed in a c(2x2) structure (as indicated by LEED), but rotated 90° from its orientation in fig. (a), such that the terminal Cl-O bond is tilted along the [1$\bar{1}$0] direction, as prescribed by the observed O$^+$ ESDIAD emission.[13]

The models of fig. 3 are intended to illustrate the coordination of perchlorate to the surface (e.g., tridentate vs. bidentate or monodentate) and the tilting of the outwardly pointing Cl-O bond from the surface normal. The exact surface bonding sites of perchlorate are as yet unknown, but the models of fig. 3 indicate the bonding sites expected on the basis of maximum coordination of the oxygen atoms contacting the surface with the surface atoms themselves. Tridentate coordination is chosen over monodentate because of the greater availability of coordination sites on the metal surface as compared to a single metal atom. Monodentate adsorption would also not concur with the ESDIAD results. If the perchlorate were adsorbed normal to the surface, the O$^+$ emission would appear as a halo if the molecule were rotating, as is observed for NH$_3$ on Ru(001),[16] or as six lobes if it were rigid due to the three oxygen atoms and the two-fold symmetry of the (110) surface. The only other way to conform to the ESDIAD data would be to have the Cl-O bond to the metal tilted such that only one Cl-O bond was directed away from the surface. This would require the other two

oxygen atoms to approach the surface, making the adsorption effectively tridentate. The case for bidentate adsorption is effectively ruled out on the basis of the energy loss results.
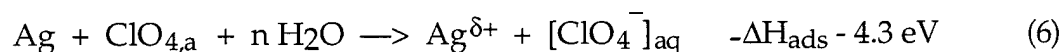
B. $ClO_4/Ag(110)$: Model Specific Adsorption

The 1220 cm^{-1} loss observed for $ClO_4/Ag(110)$ is in excellent agreement with the previously measured, in-situ IR absorption at 1218-1234 cm^{-1} for Pt(111) in perchloric acid electrolyte.[9] In accord with that study, the 1220 cm^{-1} band is assigned to the asymmetric Cl-O stretch of specifically adsorbed ClO_4. Adsorption of ClO_4 on the bare surface with trace amounts of water can then be considered a model of specific adsorption, where the ion loses part of its hydration shell in order to contact the electrode. Even though the symmetry of the perchlorate has been reduced to C_{3v} it is still slightly hydrated, as indicated by the vibrational signatures of H_2O in spectra (a) and (c) of fig. 1 and the H_2O TDS curves (a) and (c) of fig. 2.

The two, widely separated peaks for OH stretching in fig. 1(a) that residual water adsorbed along with perchlorate is hydrogen bonded in such a manner that the two O-H bonds are inequivalent. The lower energy band at 2990 cm^{-1} represents strong hydrogen bonding, which may occur by an O-H species interacting directly either with one of the oxygens of the perchlorate or with the surface. The higher energy band at 3555 cm^{-1}, which is below the gas phase O-H stretching frequencies[17,18] of 3657 and 3756 cm^{-1}, represents a weakly hydrogen bonded O-H species. No distinct H_2O scissoring mode or librational mode was observed, but this may be due to a combination of low water coverage and masking by the strong energy losses due to adsorbed ClO_4.

C. $H_2O/ClO_4/Ag(110)$: Model Non-specific Adsorption

After adsorption of H_2O to saturate the ClO_4-stabilized thermal desorption state, the Cl-O stretches at 1020 and 1220 cm^{-1} in fig. 1(a) are replaced by a single band at 1090 cm^{-1} in fig. 1(b). Reduction in the number of observed vibrational modes suggests that the C_{3v} symmetry of the tridentate ClO_4 has been increased to a more tetrahedral symmetry similar to that of aqueous perchlorate ion, shown in Table I.[12] Hydration weakens the bonds between the perchlorate and the surface such that all of the Cl-O bonds are nearly equivalent. This suggests that the water lifts the perchlorate off of the surface, producing a non-specifically adsorbed anion.

The process of forming of a non-specifically adsorbed anion is depicted in fig. 4 and can be described by the following reactions listed below along with their approximate energy requirements.

$$ClO_{4,a} \longrightarrow ClO_{4,g} \qquad\qquad -\Delta H_{ads} \qquad\qquad (2)$$

$$Ag \longrightarrow Ag^{\delta+} + e^- \qquad\qquad \Phi_m = 4.3\,eV \qquad\qquad (3)$$

$$ClO_{4,g} \longrightarrow ClO_4^-{}_{,g} \qquad\qquad -E.A. = -6.3\,eV \qquad\qquad (4)$$

$$ClO_4^-{}_{,g} + n\,H_2O \longrightarrow [ClO_4^-]_{aq} \qquad \Delta H_{hyd} = -2.3\,eV \qquad (5)$$

$$Ag + ClO_{4,a} + n\,H_2O \longrightarrow Ag^{\delta+} + [ClO_4^-]_{aq} \quad -\Delta H_{ads} - 4.3\,eV \qquad (6)$$

First, adsorbed perchlorate "desorbs" into the gas phase, as shown by eqn. (2). The energy cost of this step is the heat of adsorption of ClO_4. Because ClO_4 adsorbed on the clean surface decomposes to adsorbed Cl and O instead of desorbing molecularly, the heat of adsorption cannot be determined by thermal analysis. In eqn. (3), an electron is removed from inside the metal to just outside its surface, which is the definition of the work function[19] (Φ_m). The work function of clean Ag(110) is 4.2 eV,[20] but a value 0.1 eV

greater is used in eqn. (3) for the $H_2O/ClO_4/Ag(110)$ surface on account of the 0.1 V sample bias potential used for recording the energy loss spectrum. Of course, a more direct measurement of work function is needed to have a more accurate value. The perchlorate species and the electron then combine to form perchlorate ion in the gas phase in eqn. (4), gaining the electron affinity (E.A.) of ClO_4, which has been calculated to be 6.3 eV.[21] Finally, in eqn. (5), the gas phase ion is hydrated and gains the heat of hydration (ΔH_{hyd}). The calculated value for ΔH_{hyd} of ClO_4^- is -2.3 eV.[22] We may also obtain an estimate of the surface hydration energy from the TDS results of ClO_4-stabilized H_2O. As previously discussed[6] the ratio of peak desorption temperatures of the hydration water $T_{p,hyd}$ (190 K in fig. 2) to ice-like water $T_{p,ice}$ (162 K) approximates the ratio of the heat of hydration to the heat of sublimation (0.5 eV),

$$\Delta H_{hyd} = (T_{p,hyd}/T_{p,ice}) \Delta H_{sub}. \tag{7}$$

When eqn. (7) is applied to the TDS peak for H_2O/ClO_4,, the enthalpy of surface hydration of ClO_4 is estimated to be 0.6 eV per H_2O molecule. For the total hydration, this value must be multiplied by the solvation number. From fig. 2 the solvation number is in the range of 3-4, yielding an estimate of 1.8-2.4 eV for the hydration enthalpy, in reasonable agreement with the calculated value.[22]
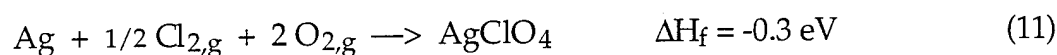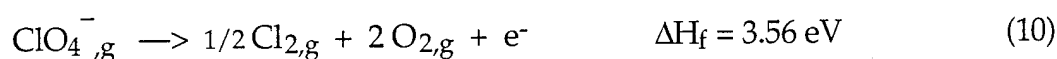
For the formation of perchlorate ion to be thermodynamically favorable, the total free energy of the reaction in eqn. (6) must be less than zero,

$$-\Delta H_{ads} + \Phi_m - E.A. + \Delta H_{hyd} \leq 0. \tag{8}$$

Although some of the calculated values are enthalpies, they can be treated as free energies if the entropic contribution is neglected because of the low temperatures in this work. The minimum value for the heat of adsorption of perchlorate in order for eqn. (6)

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to be feasible is found by solving eqn. (8); that value is $\Delta H_{ads} = -4.3$ eV.

The heat of adsorption can be estimated from the heats of formation of ClO_4^- and $AgClO_4$ as follows:

$$ClO_{4,g} + e^- \longrightarrow ClO_{4g}^- \qquad\qquad -E.A. = -6.3 \text{ eV} \qquad (9)$$

$$ClO_{4g}^- \longrightarrow 1/2\,Cl_{2,g} + 2\,O_{2,g} + e^- \qquad \Delta H_f = 3.56 \text{ eV} \qquad (10)$$

$$Ag + 1/2\,Cl_{2,g} + 2\,O_{2,g} \longrightarrow AgClO_4 \qquad \Delta H_f = -0.3 \text{ eV} \qquad (11)$$

_____

$$Ag + ClO_{4,g} \longrightarrow AgClO_4 \qquad\qquad \Delta H_{ads} = -3.0 \text{ eV} \qquad (12)$$

The calculated value of -3.0 eV is more positive than the lower limit determined by eqn. (8), suggesting that formation of a fully hydrated perchlorate ion is thermodynamically feasible in UHV.

For coadsorption of H_2O with 0.5 ML of ClO_4, the persistence of the Cl-O stretch at 1240 cm^{-1} of tridentate ClO_4 indicates that the ability of water to weaken the bonding of perchlorate to the metal is not unlimited. Even with coadsorption of 0.33 ML H_2O, much of the perchlorate remains adsorbed to the surface. The appearance of a second thermal desorption peak at 210 K in fig. 2(d), corresponding to a solvation energy of 0.65 eV per H_2O molecule using eqn. (7), would suggest stronger hydration of ClO_4, making full hydration of ClO_4 easier. However, the solvation number has decreased from 3-4 water molecules per ClO_4 to an almost 1:1 ratio, so the total solvation energy per ClO_4 actually decreases. The decrease in the solvation energy makes it less likely that the perchlorate would be fully solvated.

The decrease in solvation number corresponds to a decrease in the number of sites available for water adsorption. In order for water to lift the perchlorate off the surface, water must first adsorb to the metal, then diffuse along the surface to a perchlorate

molecule. If the surface is covered with ClO_4, it is more difficult for enough water molecules to adsorb and diffuse such that the perchlorate can be fully solvated. The absence of a distinct H_2O librational mode suggests that water does not adsorb as it does on the clean surface.

V. CONCLUSION

Adsorbed ClO_4 exhibits tridentate coordination on Ag(110). In conjunction with previous LEED and ESDIAD results, the vibrational data have been used to propose a model for this adsorption. Agreement between the EELS spectrum and in-situ IR shows that the adsorbed perchlorate and trace amounts of water can serve as a model for specific adsorption.

When the ClO_4-stabilized H_2O adsorption state is saturated for low coverages of ClO_4, the vibrational spectrum exhibits modes for ClO_4 and H_2O similar to those observed in aqueous solution. This suggests a weakening of the bonds between ClO_4 and the silver surface and non-specific adsorption. However, at the saturation ClO_4 coverage, perchlorate remains adsorbed to the surface due in part to the lack of free surface for water adsorption. Analysis of the thermodynamics of perchlorate hydration suggests that lifting ClO_4 at low coverage off the surface by complete hydration is feasible because of the low work function of the Ag(110) substrate, the high electron affinity of ClO_4^-, and the reasonably high heat of hydration of ClO_4^-. At the higher ClO_4 coverage, the total solvation energy decreases so the complete hydration of ClO_4 is not as thermodynamically favorable. Similar studies on other metal surfaces are needed to see if this effect extends to other metals, particularly those with a higher work function.

ACKNOWLEDGMENTS

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Table I

Comparison of internal vibrational modes (cm^{-1}) of adsorbed, complexed, and aqueous ClO_4 as a function of symmetry and geometry.

System	$ClO_{4,a}$	$M(ClO_4)_3{}^b$	$Cu(ClO_4)_2$ $\cdot 2H_2O$	$Cu(ClO_4)_2$	$ClO_{4,a}$	$[ClO_4]^-$	$Ag(ClO_4)$ $\cdot H_2O$
Symmetry	C_{3v}	C_{3v}	C_{3v}	C_{2v}	T_d	T_d	T_d
Structure	adsorbed alone	adsorbed tridentate	mono-dentate	bidentate	adsorbed, hydrated	aqueous	ionic
Reference	Fig. 1(a)	[11]	[10]	[10]	Fig. 1(b)	[12]	[11]
ν_a(Cl-O)	1220	1250-1267	1158	1245-1270	—	—	—
ν_a(Cl-O)	—	—	—	1130	1090	1110	1030-1160
ν_a(Cl-O)	1020	1000-1100	1030	1030	—	—	—
ν_s(Cl-O)	915	970-1000	920	920,948	880^d	932	930
δ(Cl-O),ρ	640	630^c	605,620 648	600,624 647,665	610^d	626	620

ν_a = asymmetric stretch, ν_s = symmetric stretch, δ = deformation, ρ = rocking.
^{b}M=Y, La, Nd, Sm, Gd or Er
^{c}average value
^{d}shoulder

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FIGURE CAPTIONS

Fig. 1 Electron energy loss spectra of coadsorbed ClO_4 and H_2O on Ag(110): a) <0.2 ML ClO_4 + 0.04 ML H_2O; b) <0.2 ML ClO_4 + 0.62 ML H_2O; c) 0.5 ML ClO_4 + 0.06 ML H_2O; d) 0.5 ML H_2O + 0.33 ML H_2O. ClO_4 coverages were determined from LEED patterns and H_2O coverages were determined from subsequent TDS shown in fig. 2.

Fig. 2 Thermal desorption spectra of H_2O coadsorbed with ClO_4 corresponding to the energy loss spectra in fig. 1.

Fig. 3 Model for tridentate adsorption of a) 0.1 ML ClO_4 and b) 0.5 ML ClO_4 on Ag(110).

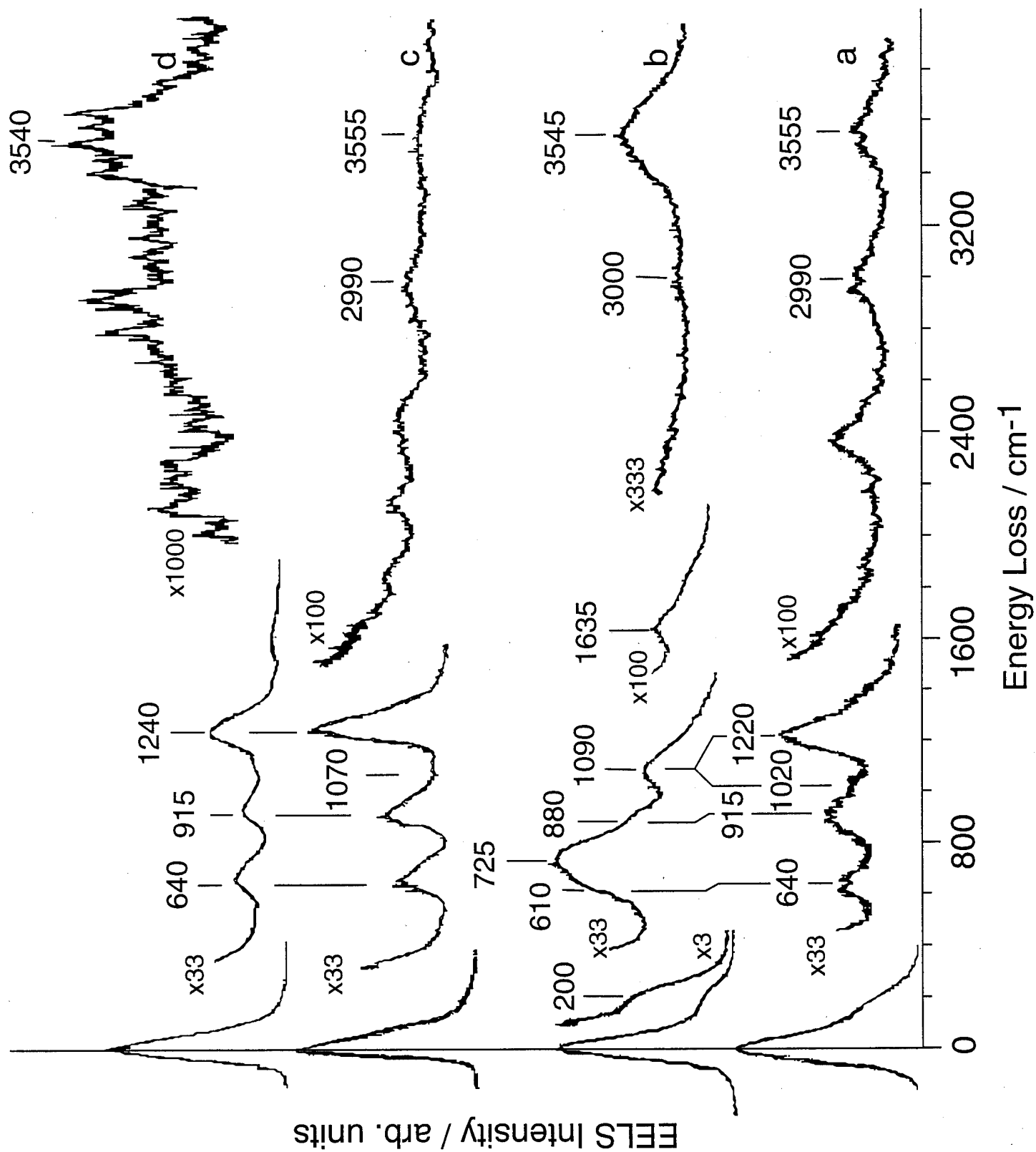Fig. 4 Born-Haber thermodynamic cycle for non-specific adsorption of ClO_4 on Ag(110).

Fig. 1, Krasnopoler and Stuve

H₂O/ClO₄/Ag(110)

Fig. 2. Krasnopoler and Stuve

O+

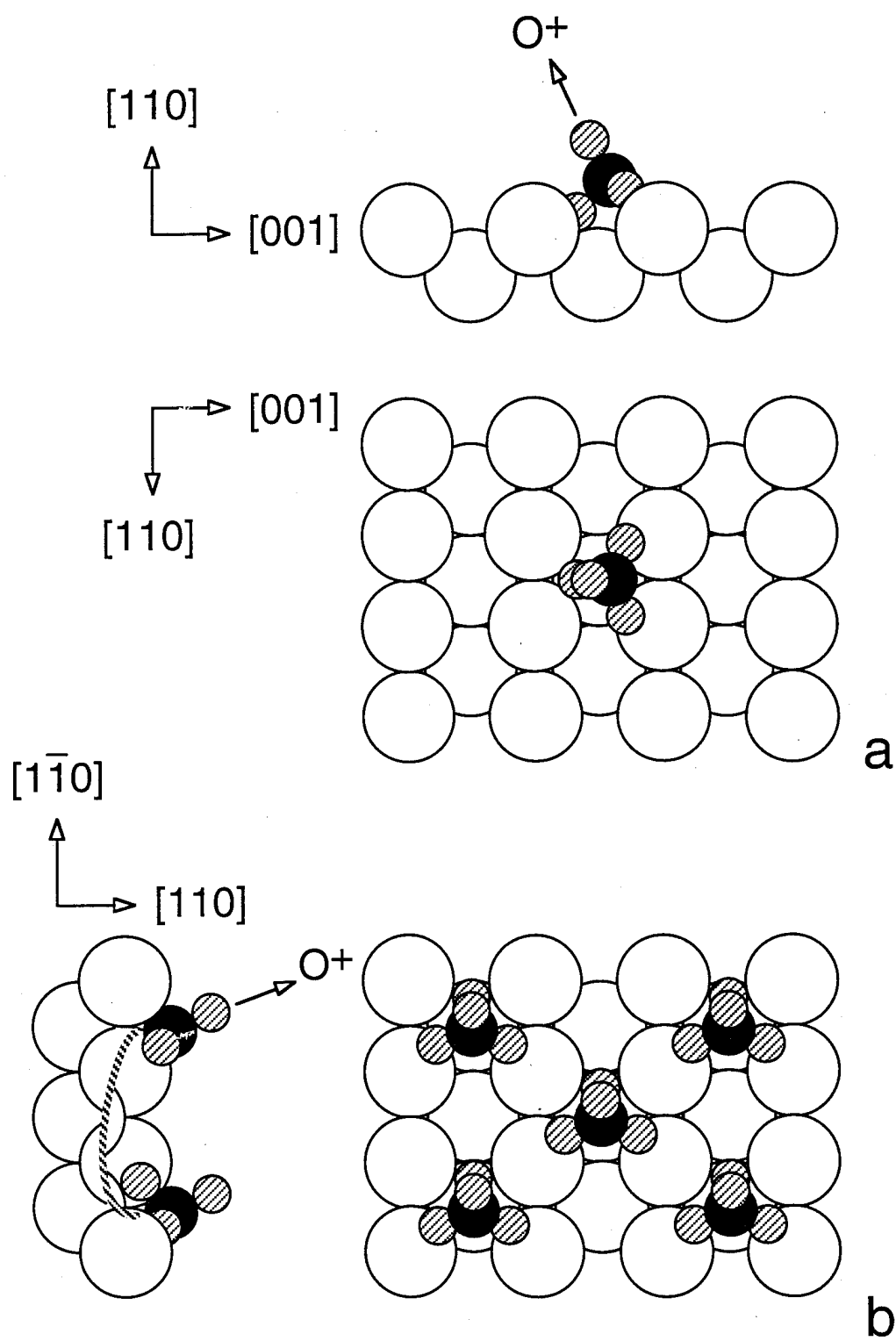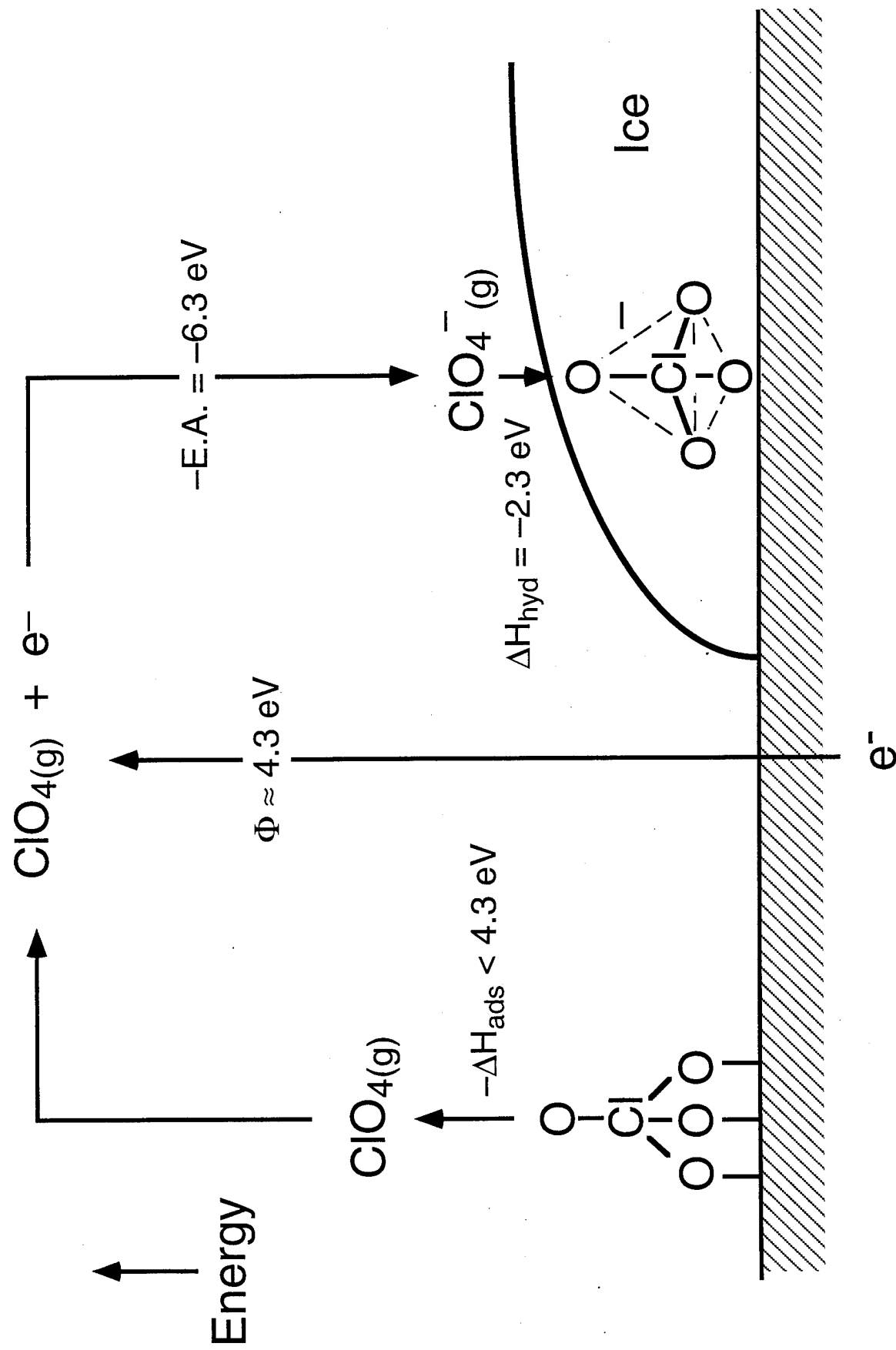[110]

[001]

[001]

[110]

a

[1̄10]

[110]

O+

b
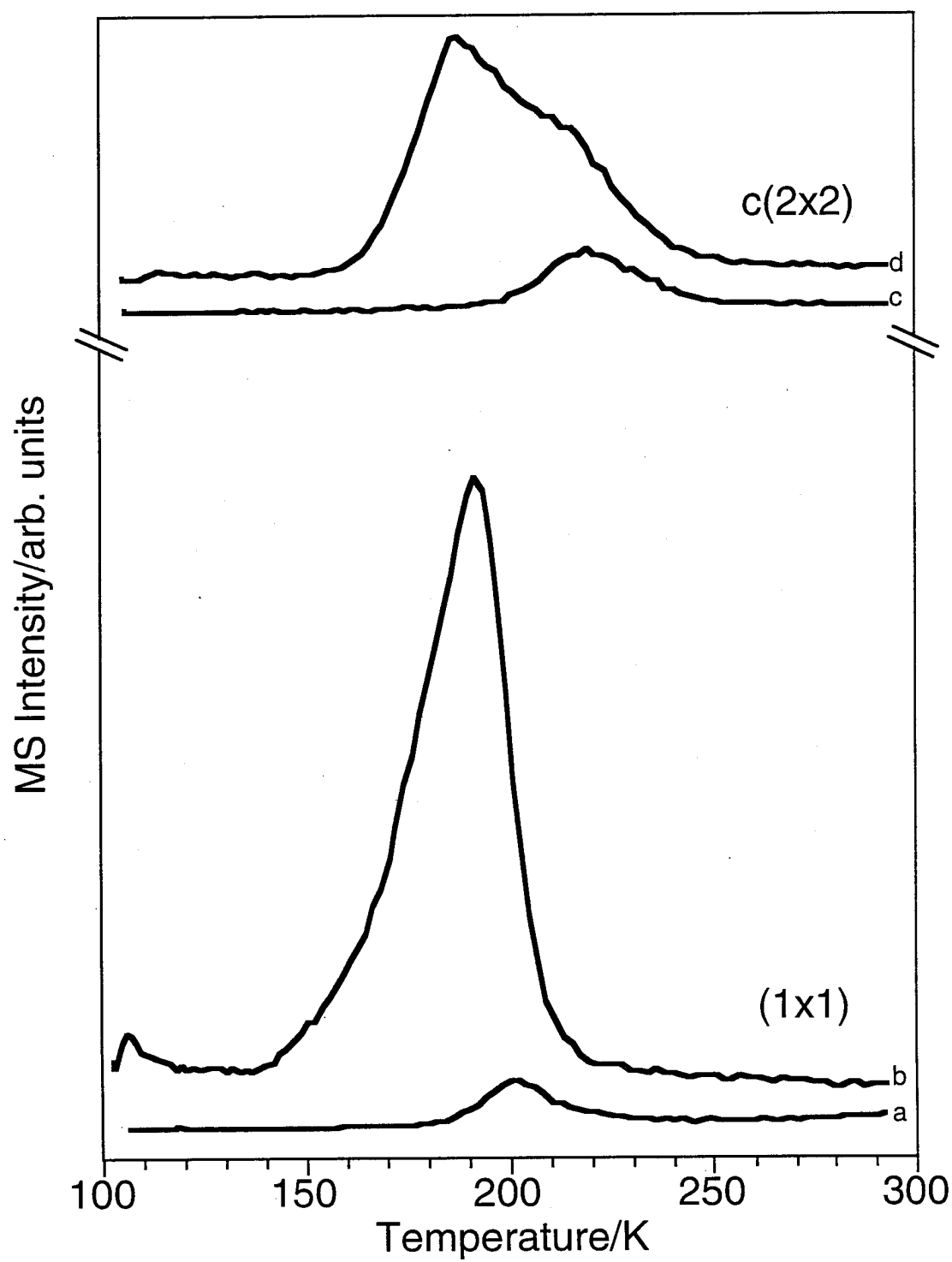
Fig. 3, Krasnopoler and Stuve

Fig. 4, Krasnopoler and Stuve